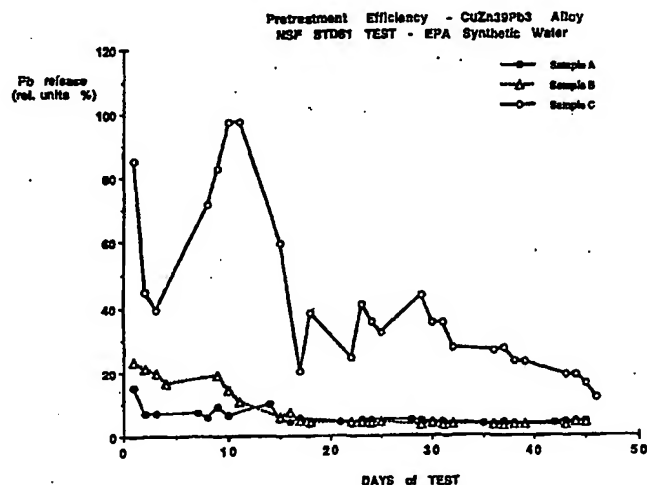


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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : E03B 7/09, C23F 1/00, C23C 22/60	A1	(11) International Publication Number: <b>WO 97/06313</b> (43) International Publication Date: 20 February 1997 (20.02.97)
(21) International Application Number: PCT/IT95/00136 (22) International Filing Date: 3 August 1995 (03.08.95) (71) Applicant (for all designated States except US): EUROPA METALLI S.P.A. [IT/IT]; Borgo Pinti, 97/99, I-50121 Firenze (IT). (72) Inventor; and (75) Inventor/Applicant (for US only): GIUSTI, Aldo [IT/IT]; Via Cesare Battisti, 15/D, I-55052 Fornaci di Barga (IT). (74) Agents: JORIO, Paolo et al.; Studio Torta, Via Viotti, 9, I-10121 Torino (IT).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, ARIPO patent (KE, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.

(54) Title: LOW LEAD RELEASE PLUMBING COMPONENTS MADE OF COPPER BASED ALLOYS CONTAINING LEAD, AND A METHOD FOR OBTAINING THE SAME



(57) Abstract

Lead brass components for potable water distribution circuits (e.g., plumbing components made of CuZn39Pb3, containing 3 % Pb), also chromium plated ones, are subjected to a lead-selective surface etching to reduce, in operation, the release of Pb caused by Pb surface "smearing", resulting either from machining or molding; said elements are firstly contacted by an aqueous solution of an acid capable of forming soluble Pb salts, preferably a non-oxidizing solution, by simply dipping the components in the solution, e.g., a solution of 0.1 M sulfamic acid, at 20°-50° C for 10 to 50 minutes, and, subsequently, the elements are passivated by immersion into a strong base aqueous solution, e.g., a solution of 0.1 M NaOH at 20°-25° C, for approximately 10 minutes; in this manner, plumbing components made of a copper based alloy containing Pb are obtained, which components, after 15 days of test according to US NSF STD61 procedure, release Pb in an amount less than 0.025 µg for each ml of the internal volume of the component delimited by metallic walls remained in contact with water during the testing period.

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- 1 -

"LOW LEAD RELEASE PLUMBING COMPONENTS MADE OF COPPER  
BASED ALLOYS CONTAINING LEAD, AND A METHOD FOR  
5 OBTAINING THE SAME."

10

#### TECHNICAL FIELD

The present invention relates to low lead release plumbing components  
15 made of copper-based alloys containing lead, e.g lead brass components for  
potable water distribution circuits. The invention further relates to a method for  
obtaining the same by a selective surface etching thereof in order to either  
reduce or completely eliminate the labile surface Pb layer (almost exclusively  
consisting of Pb and/or Pb salts) responsible for the Pb release and representing  
20 the so-called Pb surface "smearing".

#### BACKGROUND ART

Well known is the phenomenon leading to the creation of surface layers  
of metallic Pb (or of its salts), by segregation of Pb from the base alloy as a  
consequence of the thermal-mechanical stresses caused by machining and or

- 2 -

molding of brass alloy elements containing lead. Such a phenomenon is a particularly undesirable one, in that the creation of the said lead surface layer may easily cause, at work, the release into the environment of Pb ions, a heavy metal known to be highly polluting and toxic to human health.

5           On the other hand, plumbing components such as mechanic parts for cocks and valves designed to operate in potable water distribution circuits and systems, cannot but undergo, during the manufacturing process, a number of machine work operations (lathing, drilling, threading, etc.). Moreover, a Cu-Zn base alloy containing also limited amounts of Pb (generally up to 3-5 % by  
10 weight) facilitates machine working and leads to more effective and accurate surface finish. Furthermore, besides facilitating machine working (it furthers chip-breaking), the presence of Pb is also instrumental to the elements forming process, whether the latter is carried out directly by smelting or by molding/die-casting.

15           The mechanism of Pb release has long been investigated and is based on the creation, on a zinc oxide surface layer, segregated from the base alloy, of Pb salts (hydroxycarbonates), due to surface stresses of the alloy as a consequence of both machining and shear stress during the molding process, and due further to Pb reactivity with water vapor and atmosphere carbon dioxide. It is however  
20 only very recently (March 1995) that a Certified testing procedure for evaluating the Pb release of plumbing components designed to potable water distribution has been approved and issued in print by the major United States Normalization Agency, i.e. N.S.F. The test procedure is known as U.S. NSF

- 3 -

STD61. It has been shown that the phenomenon of Pb release is largely present in the commercial components for potable water distribution of any type, even in those components wherein surface coating, for example chromium or nickel plating, is extensively carried out, for haestetical reasons, on all the surfaces in view: in fact, the phenomenon depends on those limited surfaces designed to remain in contact with water when the taps, cocks ect. are closed, which are internal surfaces not in view and, therefore, normally not coated and, anyway, very difficult to be coated properly.

#### DISCLOSURE OF INVENTION

The aim of the present invention is therefore to furnish low lead release components made of copper-based alloys, in particular brass plumbing components for potable water distribution circuits, which, at the same time, can be subjected to usual working operations, by machining and/or molding, without any drawback with respect to the known alloys containing lead.

The present invention accordingly relates to mechanical components made of a copper-based alloy and adapted to be subjected, during their production stage, to working operations carried out either by machining, molding or die-casting, in particular plumbing components made of brass alloys and designed for potable water distribution systems, characterized in that said copper-based alloy contains a predetermined amount of lead as an alloying element; and in that, in combination, respective surfaces of the components designed to be exposed, in use, to any fluid released in the environment, are substantially free from lead and lead salts.

In particular, said components are designed to collect potable water

- 4 -

therein and are able to release in synthetic drinking water, after 15 days of test according to U.S. NSF STD61, an amount of Pb of no more than 0.025  $\mu\text{g}$  for each ml of the internal volume of the components delimited by metallic surfaces exposed to contact with potable water during testing.

5           It is also included in the invention, according to a further aspect thereof, a mechanical component made of a copper-based alloy containing lead, and subjected, during its production stage, to working operations carried out either by machining, molding or die-casting, in particular a plumbing component made of brass and designed for potable water distribution systems, characterized in  
10   that respective surfaces of said component, which surfaces are designed to be contacted in use by potable water, present, under XPS surface analysis, an atomic surface composition such that the surface content in Pb is lower than or equal to the content in Pb according to the nominal composition of the alloy.

          The invention further relates to a method for obtaining low Pb-release  
15   metal components made of copper-based alloys containing lead and designed to be employed in water distribution systems, in particular lead brass plumbing components for potable water circuits, said method comprising the following steps:

- a selective etching of surfaces of said components designed to be exposed, at  
20   work, to the water, for removing almost entirely the Pb and Pb salts present thereon as a consequence of a mechanical working and/or of molding/die-casting operations carried out onto said components; and

- 5 -

- a passivation of said surfaces.

In particular, the selective etching step is carried out by exposing said surfaces to the action of a non-oxidizing acidic aqueous solution, of an acid capable of forming soluble Pb salts.

5 In particular, said acid is selected from the group consisting in: sulfamic acid, fluoboric acid, methanesulfonic acid, fluosilicic acid, acetic acid and mixtures thereof

According to another embodiment of the invention, the selective etching step is carried out by exposing said surfaces to the action of an oxidizing acidic aqueous solution of an organic acid mixed with a peroxide. Preferably, the  
10 organic acid employed is citric acid and the peroxide is hydrogen peroxide.

Said passivation step follows said selective etching step and is carried out by exposure of said surfaces to the action of a basic aqueous solution, preferably a strong base aqueous solution.

15 Between said two steps, there is also provided for an intermediate rinsing stage.

Preferably, the basic aqueous solution contains a strong base selected from the group consisting in: NaOH, sodium silicate, and mixtures thereof; and the passivation step is carried out keeping the solution to a pH comprised  
20 between 10 and 13.

Said exposure operations are carried out, according to the invention, by simply dipping said components into said treating solutions; while said rinsing operations are carried out by immersion in tap water at ambient temperature.

- 6 -

Moreover, during said exposure to the action of said solutions, said solutions are subjected to ultrasonic agitation, in order to hit said surfaces of the components with ultrasonic waves.

In so doing, the ensuing selective etching of the surface lead, segregated  
5 from the alloy, affects, however, neither alloy composition nor surface finish resulting from machining (or from any other kind of working) to which said components have been subjected. Said etching operation, therefore, causes the surface lead, segregated from the alloy, to be removed so that lead is no longer released, during operation, by the elements so treated. Moreover, the removed  
10 lead can be easily recovered from the etchant, for example, by electrolysis, particularly in the presence of acid aqueous solutions. The afore process, therefore, guarantees high environmental safety.

The following passivating step, moreover, contributes to create on the exposed surfaces of said components an insoluble layer of corrosion chemicals  
15 which prevents both any possible corrosion process to be started in operation on the treated components, even in presence of aggressive fluids such as "soft waters" (potable waters having low contents of dissolved salts, especially of calcium), and the possible dissolution of the Pb not eliminated by the selective etching step (normally left inside open pores of the metallic matrix, which are  
20 deemed to be closed by the insoluble layers created by the passivation step.

Molarity range of the non-oxidizing acid, capable of forming soluble Pb salts, in the aqueous solution according to the invention, is 0.01-5 M and, in any case, its values are within the limits of the solubility scale of the chosen acid,



- 7 -

while said solution has pH range 1-3. During immersion, according to the invention, the non-oxidizing acid etching solution is kept at a temperature ranging between 20°C and 50°C and immersion is carried out for 5 to 50 minutes.

- 5        According to the preferred embodiment, the machined elements, to be treated according to the invention, are degreased, rinsed, then dipped, for a period of time not exceeding 25 minutes, into a first aqueous solution of 0.1 M sulfamic acid, at 35°C - 45°C, then subjected to further rinsing, dipped into a second aqueous solution of 0.1 M sodium hydroxide, at 20°C - 25°C and for a  
10      period of time not exceeding 15 min., and, finally, rinsed a third time and dried.

Rinsing is carried out in common tap water, at ambient temperature (13°C - 20°C).

- Finally, the preferred composition of the acidic aqueous solution is a mixture of 0.1 M sulfamic acid and 0.1 M fluoboric acid, in a 1:1 ratio,  
15      preferably added with a corrosion inhibitor.

- According to a last aspect of the invention, therefore, it is provided an aqueous solution for performing a selective Pb etching mechanical components made of copper-based metal alloys containing Pb, the selective etching being directed against a surface enrichment in Pb and Pb salts of respective surfaces  
20      of said components which have been subjected to working operations carried out either by machining, molding or die-casting, said treating solution being characterized in having the following composition:

- 0.1 M sulfamic acid;

- 8 -

- 0.1 M fluoboric acid;
- from 0.1 to 5 % by weight of 1H-benzotriazole.

It is also included in the invention, a treating aqueous solution for performing the passivation of surfaces of mechanical components made of copper-based metal alloys containing Pb, said solution being characterized in  
5 containing, in combination: 0.1 M NaOH and from 1 to 5% by weight of sodium metaphosphite. The solution also includes sodium metasilicate, and /or a surface wetting agent, e.g. polyetoxyalcohol.

#### BRIEF DESCRIPTION OF DRAWINGS

- The present invention will be further described hereinafter with reference  
10 to the following examples and the attached figures, wherein:
- figures 1 and 2 are microphotographs showing the superficial aspect of drawing wires in CuZn37Pb3 (according to CEN codification) of 5.15 mm diameter, annealed and not pickled, the white spots being the segregations of Pb and Pb salts due to the stresses caused by working the wires;
  - 15 - figures 3 and 6 are microphotographs of the same wires showing the superficial aspect of the alloy after the wires have been treated according to a first embodiment of the method of the invention, using different non-oxidizing acidic solutions;
  - figure 4 is a microphotograph showing the superficial aspect of the same wires  
20 of figures 1 and 2 after treatment with a solution of citric acid;
  - figure 5 is a microphotograph of the same wire of figure 4 treated with an oxidizing solution of citric acid, according to a second embodiment of the method of the invention;

- 9 -

-figures 7 to 10 show graphically the results of the Pb release tests carried out

according to the examples given.

# **BEST MODE OF CARRYING OUT THE INVENTION**

## **EXAMPLE 1 (copper alloys)**

Five not etched samples identified as A, B, C, D, and E, are obtained from 5,15  
5 mm diameter drawn annealed wire in CuZn37Pb3 (according to CEN denomination).

Sample A, examined by a scanning electron microscope (SEM) gave the results shown in figures 1 and 2. Thereafter, samples B, C, D and E were treated following the procedures collected in Table 1.

10

**TABLE 1**

<i>Sample</i>	<i>Solution</i>	<i>T[°C]</i>	<i>time [minutes]</i>
<b>B</b>	35% Methane sulfonic acid+ ultrasonic agitation	50	10
<b>C</b>	12% citric acid	50	10
<b>D</b>	12% citric acid + 1% $H_2O_2$	22	10
<b>E</b>	10% acetic acid	22	50

After treatment, rinsing in water and drying with hot air, samples B, C, D and E were examined by SEM technique giving the results reported in figures 3 to 6, respectively. From these micrographies, it appears that methanesulfonic acid and  
15 acetic acid are effective in selectively dissolving the surface smeared lead, while citric acid is effective if used in conjunction with an oxidizing agent, as e.g. hydrogen peroxide.

## **EXAMPLE 2 (copper alloys)**

- 10 -

Three samples, identified as A, B and C, were taken from the same bar in CuZn39Pb3, extruded and drawn to 50 mm diameter, normally available in commerce. All samples were drilled and machined with lathe turning operation, under the same working conditions, in order to obtain 100 mm high cylinders with internal diameter of 36 mm and external diameter of 50 mm. All samples were degreased and washed with tap water, Sample C was subjected to lead selective dissolution by:

- 1- immersion in solution "a": 0.1 M sulfamic acid (pH 1.25), at 40° C for twenty minutes;
- 2- washing with water;
- 3- immersion in solution "b": 0.1 M NaOH (pH 12.7) at 40° C for ten minutes;
- 4- washing with water and hot air-drying.

The overall amount of lead and copper recovered from solutions "a" and "b" per square decimeter of treated surface came to 11.4 mg and 0.1 mg, respectively.

Sample B was subjected to steps (1) and (2) only of the aforescribed procedure, then dried with hot air.

Inner surfaces of samples A, B and C were analyzed using X-ray photoelectron spectroscopy (XPS) surface analysis technique giving the results for surface atomic composition reported in Table 2.

TABLE 2

Surf.comp. [% atomic]	Sample A	Sample B	Sample C
Cu	8.4	77.4	72.6
Zn	44.9	17.0	22.6
Pb	46.7	5.7	4.8

- 11 -

Samples A, B and C were then subjected to a test for the release of metallic ions in synthetic tap water, according to protocol NSF STD61, and using the synthetic water as described in the same protocol. Lead release mean values, recorded in the first 50 days of the test are shown in Fig. 7; according thereto, the amount of lead, released by sample C, treated according to the present invention, is less than 10% of the amount of lead released by sample A during the initial period of test. By comparing the plots for samples A, B and C, it is also evident the effect of step (3), which produces a passivation of the brass surface in contact with water, lowering lead release just from the beginning of the release test.

#### EXAMPLE 3 (copper alloys)

Four samples A, B, C and D from the same bar in brass CuZn39Pb2 brass, normally extruded and drawn to 50 mm diameter, normally available in commerce, were drilled and machined with lathe turning operation, under the same working conditions, obtaining 100 mm high cylinders, with internal diameter of 36 mm and 50 mm external diameter. All samples were degreased and washed with tap water.

Samples A and B were subjected to lead-selective dissolution by:

- 1- immersion in solution "a": 0.1 M fluoboric acid at 40° C for twenty minutes;
- 2- washing with water;
- 3- immersion in solution "b": 0.1 M NaOH at 20° C for ten minutes;
- 4- washing with water and hot air-drying.

- 12 -

The overall amount of lead and copper recovered from solutions "a" and "b" per square decimeter of treated surface came to 7.3 mg and 0.1 mg, respectively.

Sample B was subjected only to steps (1) and (2) of the aforescribed procedure, then dried with hot air.

- 5 All samples were then subjected to a test for the release of metallic ions in synthetic tap water, according to protocol NSF STD61, and using the synthetic water as described in the said protocol for samples A and C, and tap water from the local water supply for samples B and D. Lead release values were recorded in the first 15 days of the release test showed that the amount of lead, released
- 10 by sample A was equal to 10% of the amount released by sample C, and the amount of lead released by sample B was equal to 15% of the amount released by sample D.

#### EXAMPLE 4 (plumbing components)

- Two samples A and B, of commercial brass ball valves, normally utilized as
- 15 parts in water supply systems, were washed and degreased. Said samples shown an internal volume  $V_i$ , defined by the volume delimited only by metallic surfaces always in contact with water, of 27 ml. Only sample A was previously subjected to lead-selective dissolution by:

- 1- immersion in solution "a": 0.1 M sulfamic acid (pH 1.25) and 2% by weight
- 20 1H-benzotriazole as corrosion inhibitor, at 40° C for twenty minutes;
- 2- washing with water;
- 3- immersion in solution "b": 0.1 M NaOH (pH 12.7) and 5% by weight of sodium metaphosphite as corrosion inhibitor, at 20° C for ten minutes;

- 13 -

4- washing with water and hot air-drying.

The overall amount of lead and copper recovered from solutions "a" and "b" per ml of said internal volume  $V_i$  came to 72  $\mu\text{g}/\text{ml}$  and 5  $\mu\text{g}/\text{ml}$ , respectively.

Samples A and B were then tested for metal release in synthetic drinking water following NSF STD61 protocol. Lead release mean values, recorded in the first 15 days of the release test, show that the amount of lead, released by sample A, is equal to 20% of the amount released by sample B. Further tests, carried out according to the procedure as described above, on other brass hydraulic commercial device parts, yielded comparable results, as reported in Table 3 and Figure 8.

**TABLE 3**

Lead release according to NSF STD61 test averaged  
around the 15th day of testing [  $\mu\text{g}/\text{liter of } V_i$  ]

<i>Device</i>	<i>As Comm. avail.</i>	<i>Pre-treated</i>
Ball valve	105	16
Disconnecter	50	6
Collector	89	17

15

**EXAMPLE 5 (plumbing components)**

Two samples A and B, of commercial chromium-plated brass faucets, normally available in commerce and utilized as distributors in water supply systems, were washed and degreased. Said samples shown an internal volume  $V_i$ , defined by the volume delimited only by metallic surfaces always in contact with water, of 80 ml. Only sample A was previously subjected to lead-selective dissolution

20

- 14 -

according to the present invention, using:

1- immersion in solution "a": 0.1 M sulfamic acid, 0.1 M fluoboric acid and 0.5% by weight of 1-H-benzotriazole as corrosion inhibitor, at 40°C, for twenty minutes;

5 2- washing with water;

3- immersion in solution "b": 0.1 M NaOH, 0.1 M sodium metasilicate and 5% by weight of sodium metaphosphite as corrosion inhibitor, at 20° for ten minutes;

4- washing with water and hot air-drying.

10 The overall amount of lead and copper recovered from solutions "a" and "b" per ml of said internal volume  $V_i$  came to 55  $\mu\text{g/ml}$  and 11  $\mu\text{g/ml}$ , respectively.

Faucets A and B were then inserted into a water supply system (municipal water supply system) and a daily sampling (100 ml) was carried out from each tap, in the morning, after at least 16 hours stagnation. Lead concentration values in  
15 these samples were recorded in the first 15 days of operation. Such results show that the amount of mean released lead from samples taken from faucet A was equal to 26% of the mean amount registered in samples taken from faucet B.

After the completion of this fifteen days release test, samples of 100 ml of water were drawn from A and B faucets after 8, 16 and 72 hours stagnation  
20 and after a flowing period of 10 minutes (these last values were taken as "zero time" points and subtracted as "blanks"). Lead concentration in all samples was determined by atomic absorption spectrometry and the results are shown in Figure 9, and confirm that faucets A, pretreated according to the present



- 15 -

invention, yields a significant better performance than commercial untreated faucet.

EXAMPLE 6 (copper alloys)

Two samples, identified as A and B, were taken from the same bar in "Gun Metal 85-5-5-5" (a copper based alloy of nominal composition, by weight: 5% lead, 5% zinc, 5% tin and 85% copper) extruded and drawn to 50 mm diameter, normally available in commerce. Both samples were drilled and machined with lathe turning operation, under the same working conditions, in order to obtain 100 mm high cylinders with internal diameter of 36 mm and external diameter of 50 mm. Both samples were degreased and washed with tap water.

Sample A, according to the present invention, was subjected to lead selective dissolution by:

- 1- immersion in solution "a": 0.1 M sulfamic acid and 0.1 M fluoboric acid at 40°C for 25 minutes;
- 2- washing with water;
- 3- immersion in solution "b": 0.1 M NaOH, 0.1 M sodium metasilicate and 5% by weight of sodium metaphosphite, at 20°C for 10 minutes;
- 4- washing with water and hot air drying.

The overall amount of lead and copper recovered from solutions "a" and "b" per square decimeter of treated surface came to 285 mg and 1.8 mg, respectively.

Inner surfaces of A and B samples were analyzed using X rays photoelectron spectroscopy (XPS) surface analysis technique giving the results for surface

- 16 -

atomic composition reported in Table 4.

TABLE 4

<i>Surf. comp. [atomic %]</i>	<i>Sample A</i>	<i>Sample B</i>
<b>Cu</b>	83.9	53.0
<b>Zn/Sn</b>	2.8	4.0
<b>Pb</b>	13.3	43.1

EXAMPLE 7 (plumbing components)

5 Two samples, A and B, of commercial chromium plated brass faucets, normally available in commerce and utilized as distributors in water supply systems, were washed and degreased. Said samples shown an internal volume Iv, defined as the volume delimited only by metallic surfaces always in contact with water, of 200 ml. Only sample A was previously subjected to lead selective dissolution  
10 according to the present invention, using:

1- immersion in solution "a": 0.1 M sulfamic acid, at 40°C for 25 minutes;

2- washing with water;

3- immersion in solution "b": 0.1 M NaOH, 5% by weight of sodium metaphosphite (corrosion inhibitor) and 0.5% by weight of polyetoxyalchool (as

15 a surface wetting agent), at 20°C for 10 minutes;

4- washing with water and hot air drying.

The overall amount of lead and copper recovered from solutions "a" and "b" per ml of said internal volume Iv came to 440 µg /ml and 33 µg/ml, respectively.

20 Faucets A and B were then tested for metal release in syntethic drinking water

- 17 -

following NSF STD61 protocol for four weeks. Lead release mean values recorded during the first 15 days of test show that lead release for pretreated faucet A is 35% of lead release observed for faucet B. At around the 15th day of the test, the lead release from faucet A is about 21  $\mu\text{g/l}$  of Iv volume, while  
5 for faucet B the figure is around 80  $\mu\text{g/l}$  of Iv volume. Figure 10 shows results obtained during the four weeks lead release test for faucets A and B.

- 18 -

CLAIMS

1. Mechanical components made of a copper-based alloy and adapted to be subjected, during their production stage, to working operations carried out either by machining, molding or die-casting, in particular plumbing components  
5 made of brass alloys and designed for potable water distribution systems, characterized in that said copper-based alloy contains a predetermined amount of lead as an alloying element; and in that, in combination, respective surfaces of the components designed to be exposed, in use, to any fluid released in the environment, are substantially free from surface enrichment of lead and lead  
10 salts.
2. Mechanical components as claimed in Claim 1, wherein said components are designed to collect potable water therein, characterized in that the components are able to release, after fifteen days of NSF STD61 release test with synthetic drinking water, an amount of Pb of no more than 0.025 µg for  
15 each ml of the internal volume (Iv) of the components delimited only by metallic surfaces exposed to contact with said drinking water during the testing period.
3. A mechanical component made of a copper-based alloy containing lead, and subjected, during its production stage, to working operations carried out either by machining, molding or die-casting, in particular a plumbing component  
20 made of brass and designed for potable water distribution systems, characterized in that respective surfaces of said component, which surfaces are designed to be contacted in use by potable water, present, under XPS surface analysis, an atomic surface composition such that the surface content in Pb is

- 19 -

lower than or equal to the content in Pb according to the nominal composition of the alloy.

4. A method for obtaining low Pb-release metal components made of copper-based alloys containing lead and designed to be employed in water distribution systems, in particular lead brass plumbing components for potable water circuits, said method comprising the following steps:

- a selective etching of surfaces of said components designed to be exposed, at work, to the water, for removing almost entirely the Pb and Pb salts present thereon as a consequence of a mechanical working and/or of molding/die-casting operations carried out onto said components; and
- a passivation of said surfaces.

5. A method as claimed in Claim 4, characterized in that said selective etching step is carried out by exposing said surfaces to the action of a non-oxidizing acidic aqueous solution, of an acid capable of forming soluble Pb salts.

6. A method as claimed in Claim 5, characterized in that said acid is selected from the group consisting in: sulfamic acid, fluoboric acid, methanesulfonic acid, fluosilicic acid, acetic acid and mixtures thereof.

7. A method as Claimed in Claim 5 or 6, characterized in that molarity range of the non-oxidizing acid capable of forming soluble Pb salts in the said aqueous solution, is 0.01-5 M.

8. A method as claimed in any one of the above Claims 4 to 7, characterized in that the pH range of the said aqueous solution is 1-3.

- 20 -

9. A method as claimed in any one of the above Claims 4 to 8, characterized in that the temperature of said aqueous solution of a non-oxidizing acid, capable of forming soluble Pb salts, ranges from 20° C to 50° C.
10. A method as claimed in anyone of the foregoing Claims 4 to 9,  
5 characterized in that said exposure to the action of said non-oxidizing acidic aqueous solution, capable of forming soluble Pb salts, is carried out by simply dipping said elements into the said solution for 5-50 minutes.
11. A method as claimed in Claim 4, characterized in that said selective etching step is carried out by exposing said surfaces to the action of an  
10 oxidizing acidic aqueous solution of an organic acid mixed with a peroxide.
12. A method according to Claim 11, characterized in that said organic acid employed is citric acid and the peroxide is hydrogen peroxide.
13. A method according to anyone of the foregoing Claims from 4 to 12, characterized in that said passivation step follows said selective etching step and  
15 is carried out by exposure of said surfaces to the action of a basic aqueous solution, preferably a strong base aqueous solution.
14. A method according to Claim 13, wherein the basic aqueous solution contains a strong base selected from the group consisting in: NaOH, sodium silicate, and mixtures thereof; and the passivation step is carried out keeping  
20 the solution to a pH comprised between 10 and 13.
15. A method according to anyone of the foregoing Claims from 4 to 14, characterized in that, between said two steps of etching and passivating, there is also provided for an intermediate rinsing stage.

- 21 -

16. A method as claimed in Claims from 4 to 10, characterized in that said components are degreased, rinsed, then dipped, for a period of time not exceeding 25 minutes, into a first aqueous solution of 0.1 M sulfamic acid, at 35°C - 45°C, then subjected to further rinsing, dipped into a second aqueous solution of 0.1 M sodium hydroxide, at 20°C - 25°C and for a period of time not exceeding 15 minutes, and, finally, rinsed a third time and dried.
17. A method as claimed in anyone of the above Claims from 4 to 10, characterized in that the composition of the said acidic aqueous solution is a mixture of 0.1 M sulfamic acid and 0.1 M fluoboric acid, in a 1:1 ratio.
18. A method as claimed in Claims 15 or 16, characterized in that said rinsing operations are carried out by immersion in tap water at ambient temperature.
19. A method as claimed in any one of the above Claims, characterized in that, during said exposure to the action of said solutions, said solutions are subjected to ultrasonic agitation, in order to hit said surfaces of the components with ultrasonic waves.
20. A method for obtaining low Pb-release metal components made of copper-based alloys containing lead and designed to be employed in water distribution systems, in particular lead brass plumbing components for potable water circuits, as illustrated and described with reference to the accompanying Figures.
21. A treating aqueous solution for performing a selective Pb etching mechanical components made of copper-based metal alloys containing Pb, the

- 22 -

selective etching being directed against a surface enrichment in Pb and Pb salts of respective surfaces of said components which have been subjected to working operations carried out either by machining, molding or die-casting, said treating solution being characterized in having the following composition:

5    - 0.1 M sulfamic acid;

     - 0.1 M fluoboric acid;

     - from 0.1 to 5 % by weight of 1H-benzotriazole.

22.    A treating aqueous solution for performing the passivation of surfaces of mechanical components made of copper-based metal alloys containing Pb,  
10    said solution being characterized in containing, in combination: 0.1 M NaOH and from 1 to 5% by weight of sodium metaphosphite.

23.    A treating aqueous solution as claimed in Claim 22, wherein it also includes sodium metasilicate.

24.    A treating aqueous solution as claimed in Claim 22 or 23, wherein it also  
15    includes a surface wetting agent, preferably polyetoxyalchool.



1 / 7

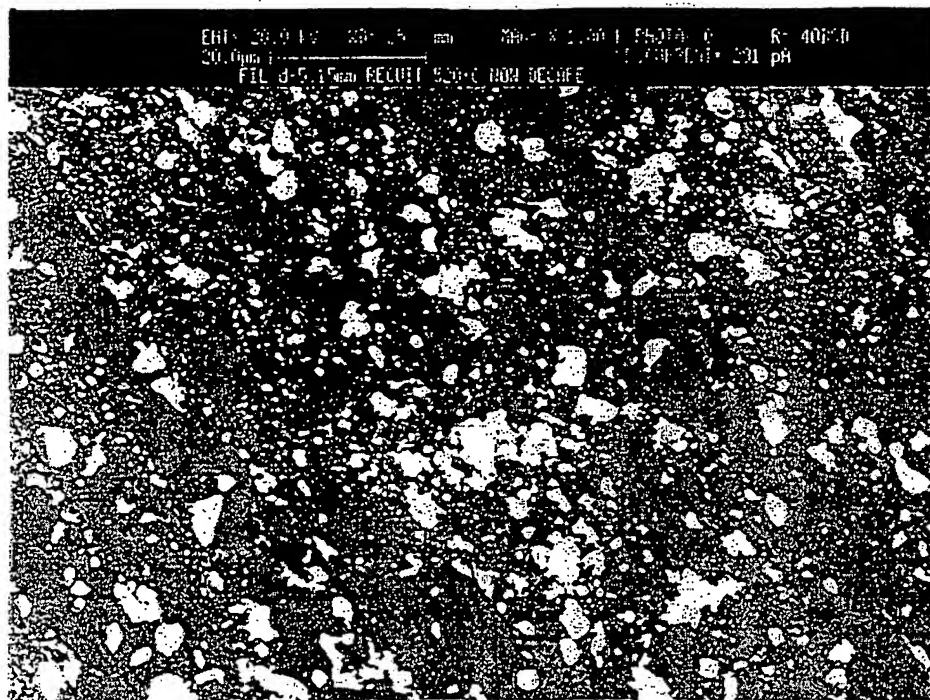


Fig. 1

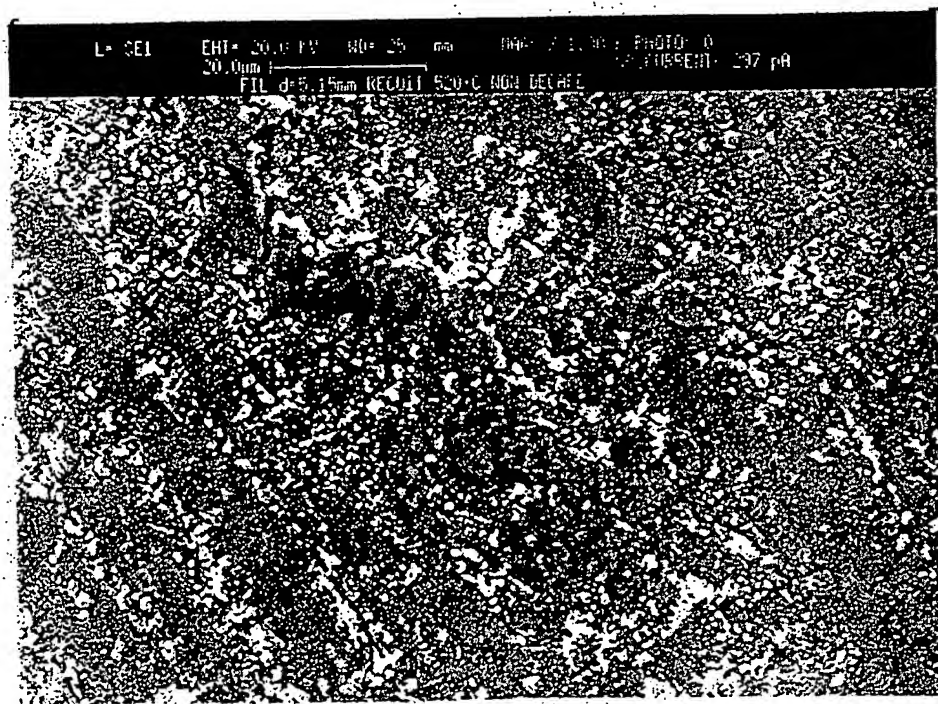


Fig. 2

217

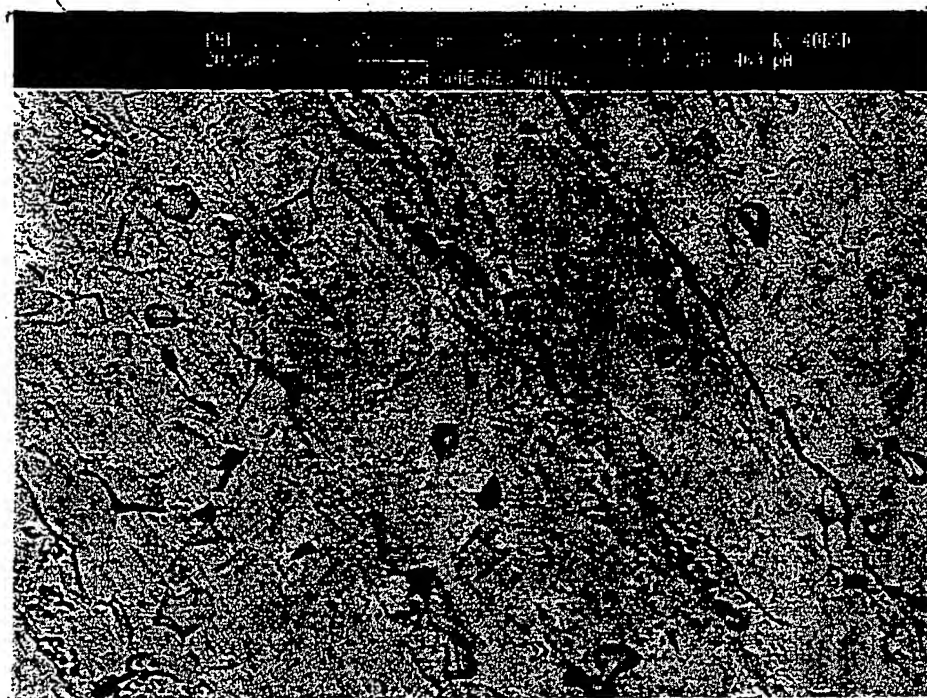


Fig. 3

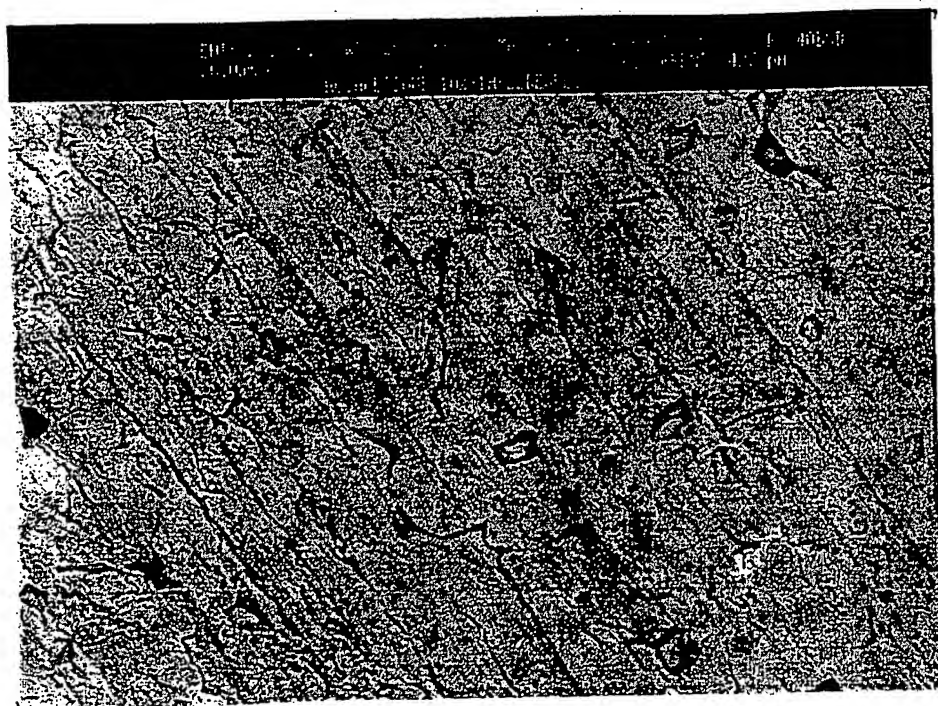


Fig. 6

3 / 7

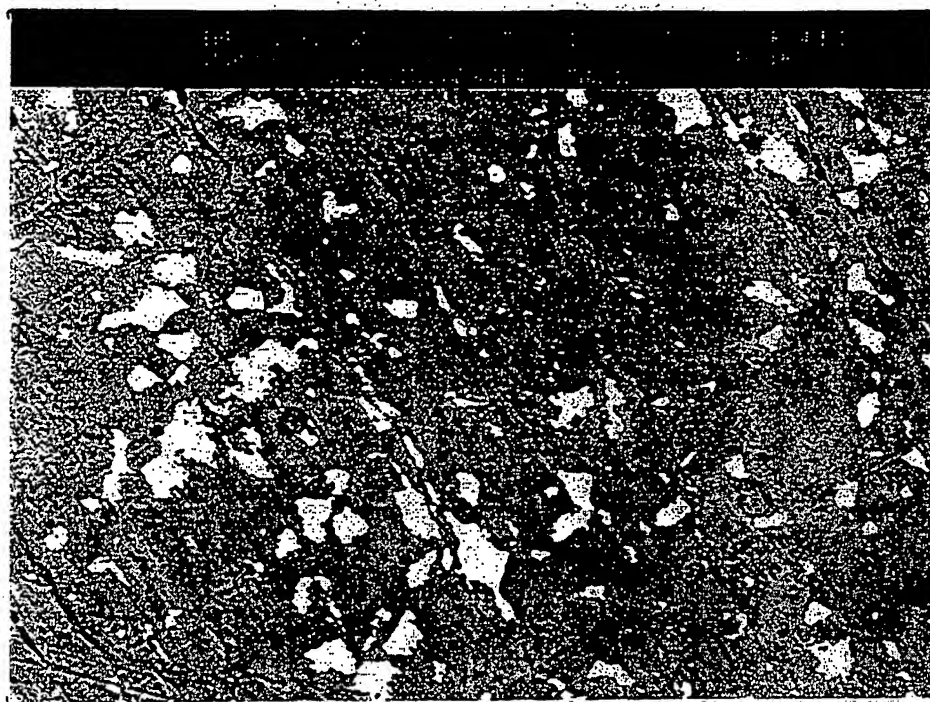


Fig. 4

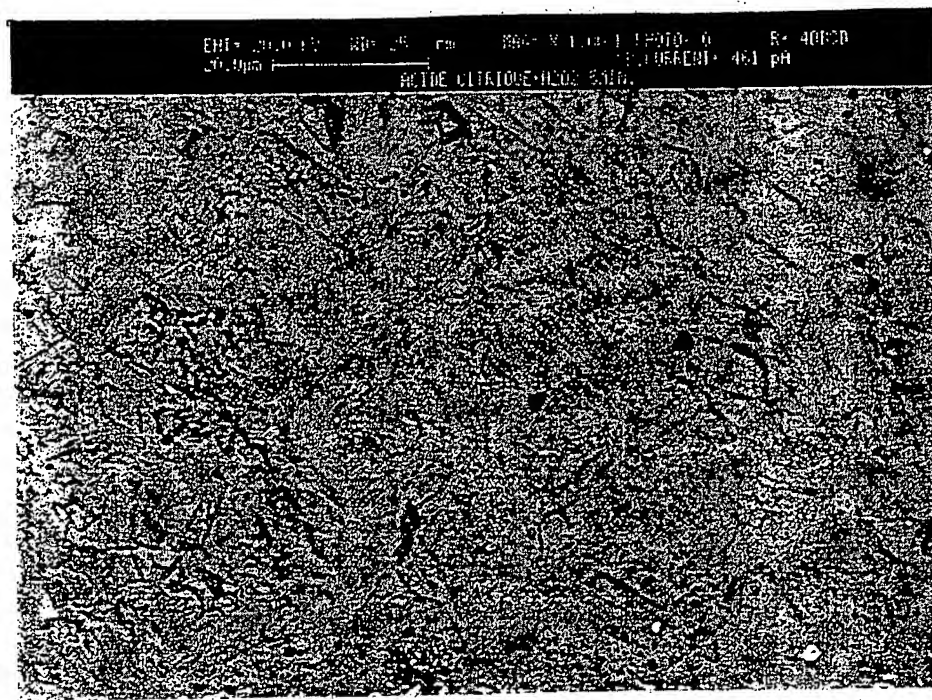


Fig. 5

4 / 7

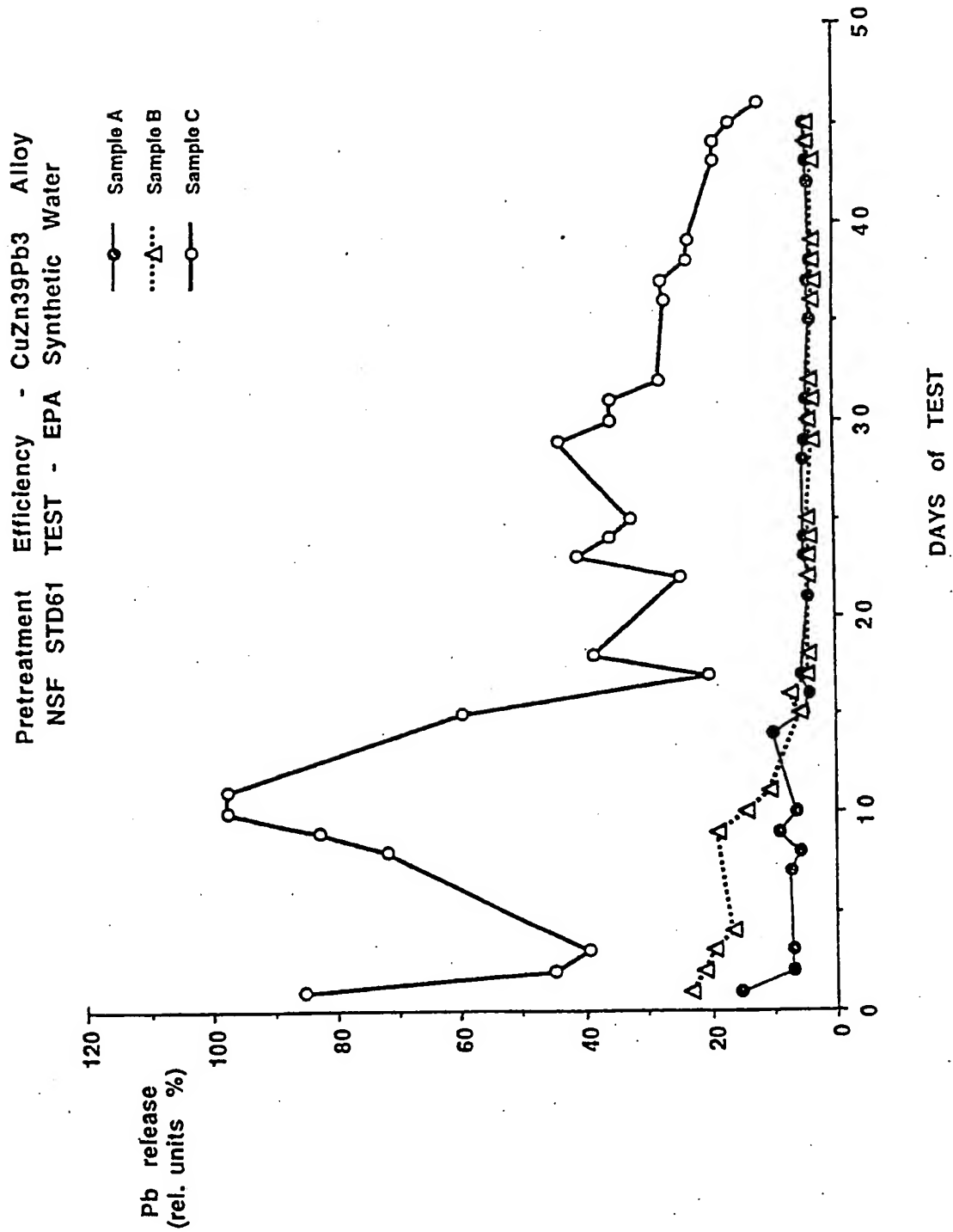


Fig. 7

5 / 7

# Pretreatment Efficiency - Commercial Plumbing Devices

NSF STD61 Test - EPA Synthetic Water

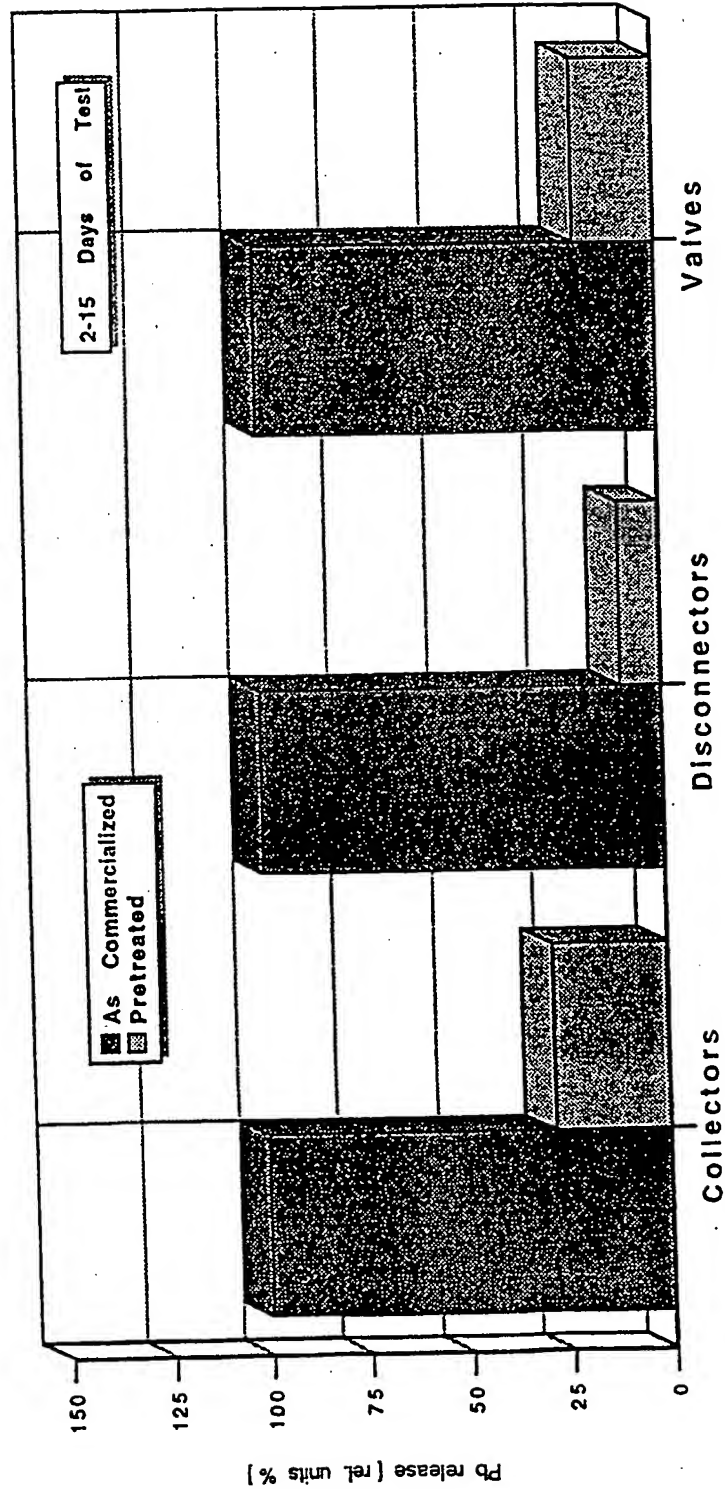


Fig.8

6 / 7

# Pretreatment Efficiency - Commercial Faucets

Tap Water after stagnation - 300/340 Hours on service

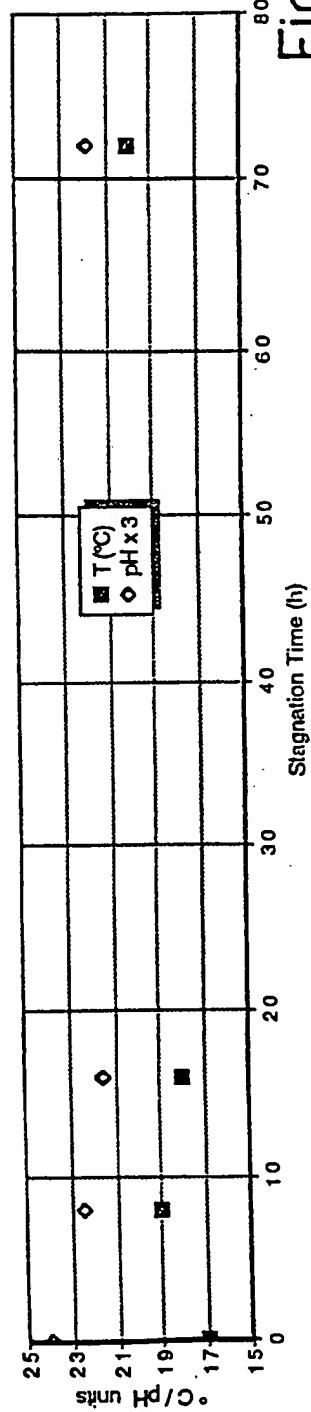
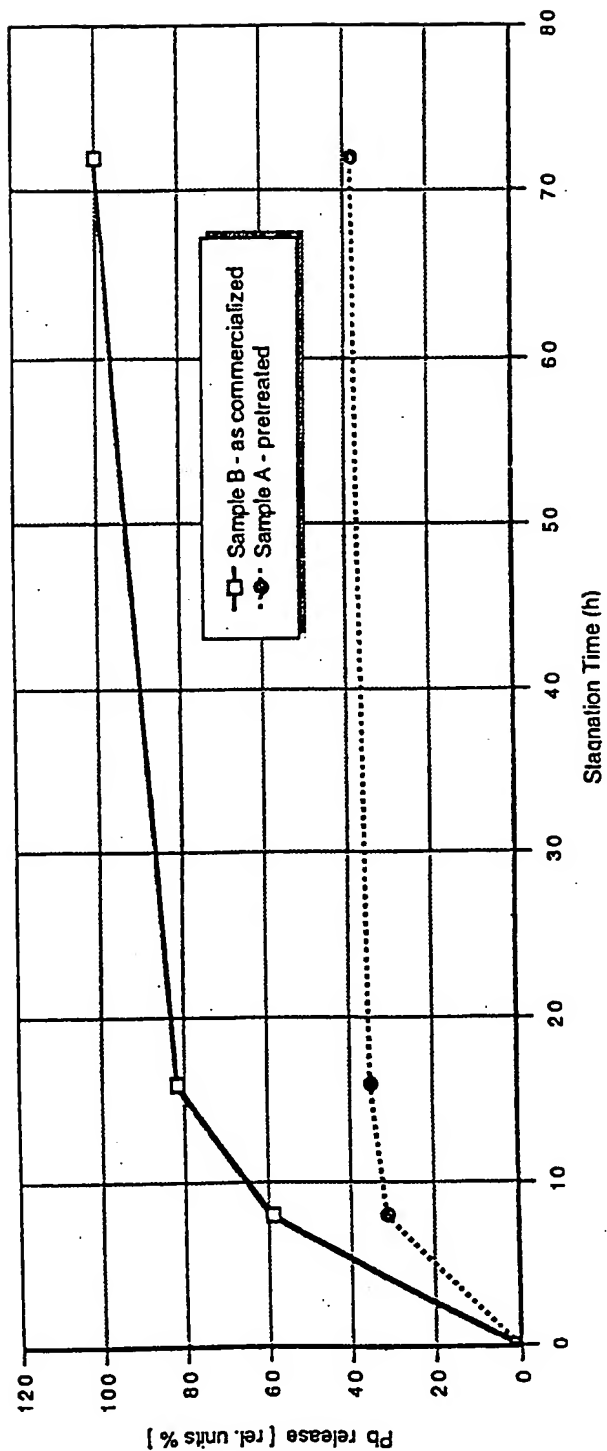


Fig.9

7/7

Pretreatment Efficiency - Commercial Faucets  
NSF STD61 TEST - EPA Synthetic Water

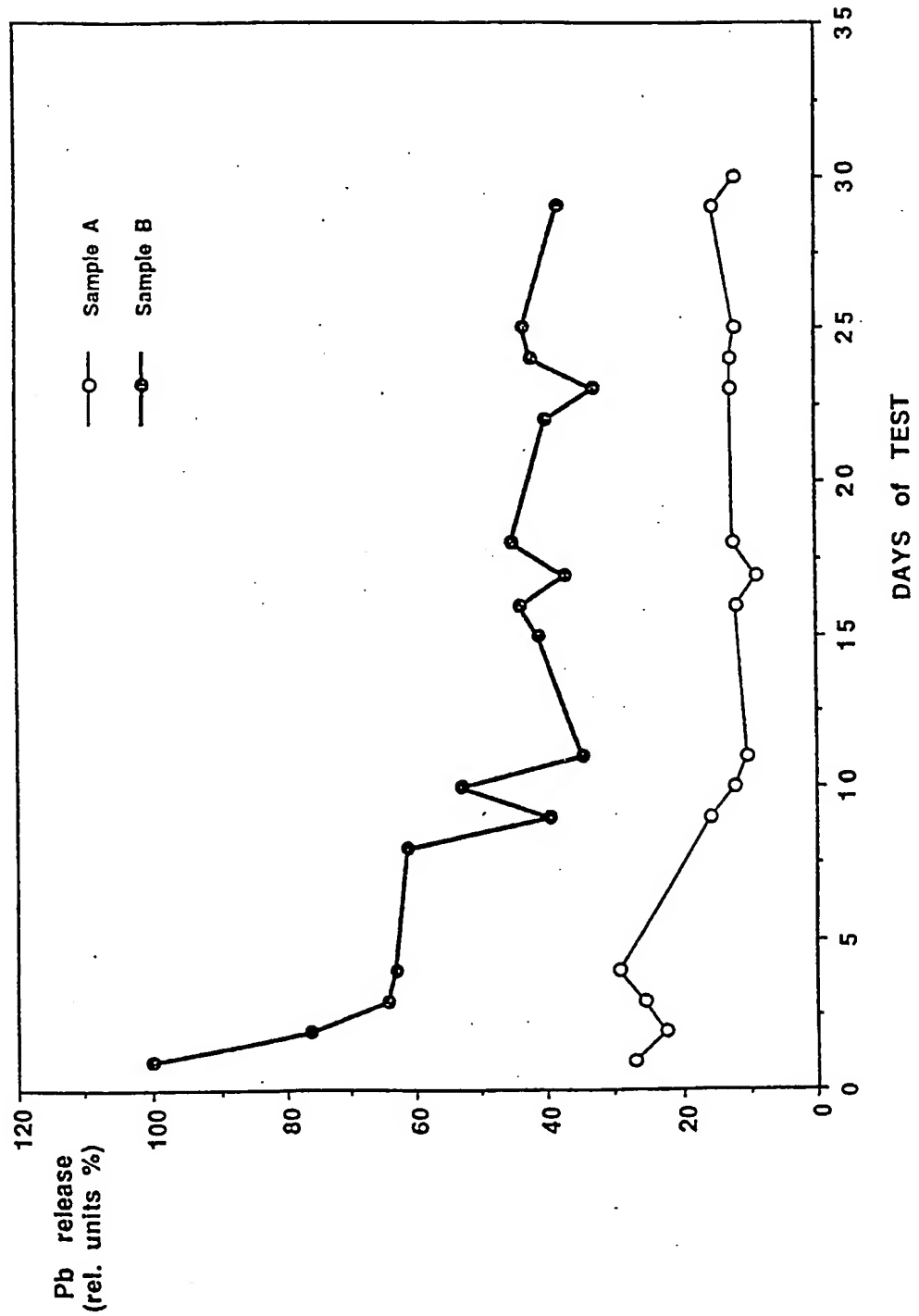


Fig.10

# INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/IT 95/00136

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 E03B7/09 C23F1/00 C23C22/60

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 E03B C23F C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,43 13 439 (IDEAL STANDARD) 27 October 1994 see column 1, line 64 - column 2, line 23; claim 1 ---	1-3
A	MATERIALS PERFORMANCE, vol. 29, no. 8, 1 August 1990 pages 45-49, XP 000175798 BOFFARDI B P 'MINIMIZATION OF LEAD CORROSION IN DRINKING WATER' see page 45, right column, line 1-16 see page 48, left column, last paragraph - page 48, middle column, line 2 ---	1-3
A	DE,A,36 19 881 (WMF WUERTTEMBERG METALLWAREN) 17 December 1987 see page 4, line 8-10; claims 1,2,15 --- -/--	4,11,12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

4 April 1996

Date of mailing of the international search report

10.05.96

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# INTERNATIONAL SEARCH REPORT

Int. Application No  
PCT/IT 95/00136

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	US,A,4 097 394 (GERLACH GIJSBERTUS ET AL) 27 June 1978 see claim 1 ---	22
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E	EP,A,0 683 245 (IMI YORKSHIRE FITTINGS) 22 November 1995 see claim 1 -----	1-4

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/IT 95/00136

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